

LARGE-SCALE POLYANILINE BATTERIES

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Summary

The electrochemical performance of polyaniline film (PANF) and polyaniline powder (synthesized chemically, (PANC), or electrochemically (PANe)) as the positive electrode material in zinc rechargeable batteries has been examined. The energy density of the different forms of polyaniline is in the order: PANF > PANe > PANC. Diffusion of reacting species has been identified as the principal factor determining the characteristics of the polyaniline powder electrode. The 1A form of polyaniline provides a slightly greater energy density than the 1S form.

Introduction

In recent years, considerable interest has been shown in the study of polyaniline as a conducting organic polymer [1, 2]. It has been found that polyaniline film (prepared electrochemically) or polyaniline powder (synthesized by chemical or electrochemical polymerization [3, 4]) exhibits several redox couples in aqueous solutions. The quasi-reversible nature of polyaniline can be utilized in aqueous secondary batteries. Although there have been several reports [5, 6] on employing polyaniline film as the positive electrode in secondary batteries, no detailed information is available on the electrochemical performance of secondary batteries with polyaniline powder electrodes. Furthermore, most of the previous studies have been conducted on electrodes of small surface area, *e.g.*, less than several cm².

Fabrication of electrodes from polyaniline powder has been found to offer many advantages: no requirement for a substrate for the polyaniline-film deposition; no limit to the amount of active material; no difficulty in electrode scale-up, etc.

In the present work, results are reported for the performance of a large-scale polyaniline powder electrode (area 20 cm²) in a rechargeable zinc cell. For comparative purposes, charge/discharge tests have also been conducted on a polyaniline film deposited on a platinum substrate (area 20 cm²).

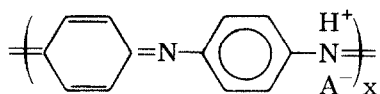
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Experimental

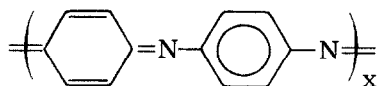
A polyaniline-film electrode (PANF) was deposited on a platinum-foil electrode (4 cm × 5 cm) by repeated cycling over a potential range -0.2 V to +0.8 V (*versus* standard calomel electrode, SCE) in a solution of 1.0 M HCl with 0.2 M aniline. The potential sweep rate was 50 mV s⁻¹.

Polyaniline powder was synthesized either by chemical or electrochemical means. The former powder is termed PANc, the latter PANe. PANc was obtained through oxidation of aniline by (NH₄)₂S₂O₈ in HCl solution of pH 1. PANe was synthesized by potentiostatic electrolysis of 0.2 M aniline in 1.0 M HCl at +0.8 V on a platinum foil electrode. The PANe powder was scraped from the electrode into a filter funnel. All PANc and PANe powders were rinsed with 1.0 M HCl solution and dried under vacuum at 90 °C for 48 h.

According to Chiang and MacDiarmid [7], the above polyaniline samples can be represented as the 1S form:



In order to determine whether proton doping provides any contribution to the cell capacity, the 1A form of polyaniline,



obtained through treating the 1S form with NaOH solution of pH 14, was also examined.

In test cells, the polyaniline-film electrode was used as-prepared. The polyaniline-powder electrode was fabricated by rolling a mixture of the powder with 20 wt.% Teflon emulsion as binder. The dimensions of the rolled sheet were 4 cm × 5 cm; the thickness varies with the amount of powder used. A platinum screen with a platinum-wire lead was pressed on to the rolled sheet and served as a current collector.

Each test cell consisted of a polyaniline positive electrode separated from a negative of zinc plate by a porous membrane. The electrolyte was saturated ZnCl₂ solution. In some cases, 1 M NH₄Cl was added to the ZnCl₂ solution.

The cells were charged at constant-current density (1 mA cm⁻²) to a cell voltage of 1.6 V. Discharging was carried out with 100 Ω constant load, unless otherwise stated. All charge/discharge tests were conducted at room temperature.

Results and discussion

Data obtained from charge/discharge tests on PANF, PANe and PANc electrodes are summarized in Table 1. These include:

- (i) constant-charge current density I_{in} , also given as the number of coulombs, Q_{in} , involved in the charge process;
- (ii) average discharge voltage, \bar{V}_d ;
- (iii) discharge time, t_{out} , for cell voltage to fall to 0.9 V;
- (iv) coulombs liberated during discharge, Q_{out} ;
- (v) coulomb efficiency: $Q_{eff} = Q_{out}/Q_{in}$;
- (vi) specific capacity and energy density of polyaniline electrode under study.

\bar{V}_d values were calculated from the area under each discharge curve divided by the total discharge time. Energy densities were determined from the formula:

$$\text{Energy density} = \bar{V}C = \bar{V} \int_0^t I dt = \bar{V} \int_0^t \frac{V}{R} dt = \frac{\bar{V}}{R} \int_0^t V dt$$

From Table 1, it can be seen that the energy density for different polyaniline forms decreases in the order: PANF > PANe > PANc. This difference in performance could be due to the different thicknesses of the individual electrodes. In order to resolve this possibility, the effect of thickness of the PANc electrode on cell performance was studied; the results are presented in Table 2. It can be seen that cell performance improves with decrease in the thickness of the electrode. This behaviour is attributed to a restricted diffusion of reacting species during discharge, so that internal areas of the polyaniline powder in the thicker electrodes do not actively participate in the reaction process.

The importance of the diffusion of reacting species in determining the electrode kinetics is further confirmed by the fact that the performance of polyaniline powder electrodes depends greatly on the discharge rate. Table 3 shows results obtained with a polyaniline powder electrode that was charged with the same number of coulombs but discharged under different loads. It is clearly seen that the discharge current affects not only the coulomb efficiency, but also the specific capacity of the electrode.

TABLE 1

Performance of polyaniline prepared by different methods

Type	Wt. (g)	I_{in} (mA cm ⁻²)	Q_{in} (C)	\bar{V}_d (V)	t_{out} (min)	Q_{out} (C)	Q_{eff} (%)	Capacity (A h kg ⁻¹)	Energy density (W h kg ⁻¹)
PANF	0.030	0.99	10.3	1.10	13.6	9.01	87.5	83.4	91.7
PANe	0.250	0.99	57.9	1.11	85	56.60	97.8	62.9	69.9
PANc	0.250	0.99	57.0	1.12	80	53.70	94.3	59.7	66.9

TABLE 2

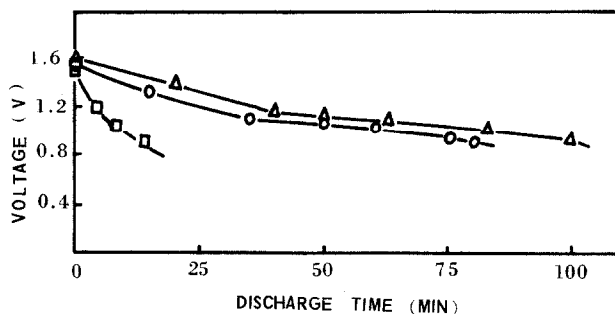
Effect of electrode thickness on cell performance

Wt. of PAnC (g)	Q_{in} (C)	\bar{V}_d (V)	t_{out} (min)	Q_{out} (C)	Q_{eff} (%)	Capacity (A h kg ⁻¹)	Energy density (W h kg ⁻¹)
2	300	1.11	445	297.3	99.1	41.3	45.5
0.5	103	1.2	122	88.2	85.6	49.0	58.8
0.25	57	1.12	80	56.6	94.3	59.7	66.9

TABLE 3

Performance of PAnC discharged under different loads

Load (Ω)	Q_{in} (C)	Q_{out} (C)	Q_{eff} (%)	Capacity (A h kg ⁻¹)	Energy density (W h kg ⁻¹)
500	58.4	58.36	99.9	64.8	73.46
200	58.4	56.1	96.1	62.3	70.61
100	58.4	53.5	91.61	59.4	67.04
50	58.4	51.2	87.6	56.9	63.50
20	58.4	38.8	66.4	43.1	45.5
10	58.4	22.1	37.8	24.6	23.54

Fig. 1. Discharge curves for: \square , PAnF; \circ , PAnE; \triangle , PAnC.

Discharge curves for PAnF, PAnE and PAnC are given in Fig. 1. Several specific redox couples can be identified; these can be associated with differences in the nature of the electrochemical reactions taking part in the corresponding potential regions.

Chiang and MacDiarmid [7] have observed proton doping in polyaniline. However, it is still unclear whether such doping contributes directly to the capacity, or only leads to the reversible conversion of polyaniline from an insulating state to a conducting state. In order to clarify the situation, a special electrochemical cell was constructed in which two compartments were divided by a special membrane of low resistance. One compartment

contained a zinc plate immersed in saturated ZnCl_2 ; the other contained a polyaniline electrode in 0.1 M H_2SO_4 . Under the latter conditions, the polyaniline is believed to be proton doped. The charge/discharge behaviour of the cell is shown in Table 4.

TABLE 4

Performance of polyaniline batteries with membrane* and with 1A form of polyaniline

Wt. (g)	Q_{in} (C)	t_{out} (min)	Q_{out} (C)	Q_{eff} (%)	Capacity (A h kg^{-1})	Energy density (W h kg^{-1})
<i>Membrane, 1S form of polyaniline</i>						
0.25	57	80	53.7	94.3	59.7	66.9
<i>1A form of polyaniline</i>						
0.25	84		77.5	92.3	86.1	92.8

*In membrane cell, voltage loss due to resistance of membrane is small.

Quite remarkably, the performance of the cell was similar to one using polyaniline in ZnCl_2 solution. This result prompted a study of the characteristics of a cell consisting of the 1A form of polyaniline in 1 M ZnCl_2 + 0.5 M NH_4Cl solution (pH 4.4). The 1A form is an insulating material and there are no peaks on the voltammogram in solutions of $\text{pH} > 3$ [8]. In fabricating electrodes from 1A polyaniline, 20 wt.% acetylene black was added to render the electrode conductive. A typical discharge curve obtained on the first cycle is given in Fig. 2. Except for the initial fall in potential, the voltammogram is essentially linear in form. This suggests that the electrochemical reaction of the 1A form of polyaniline may be more simple than that of the 1S form. One possible reaction is:

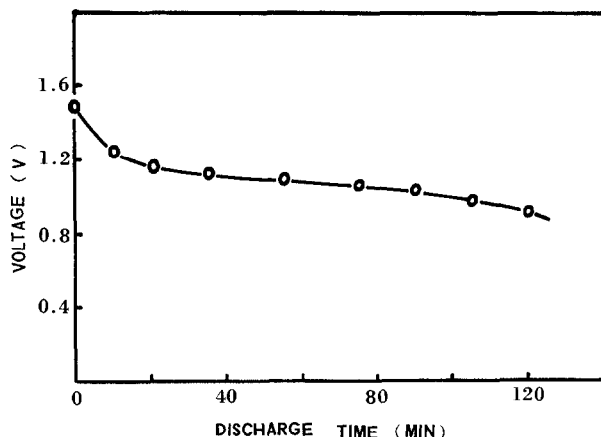
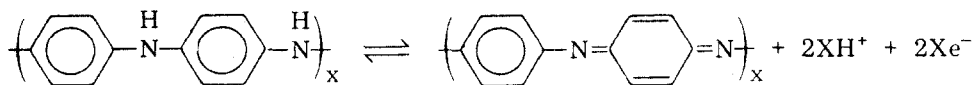


Fig. 2. Discharge curve of 1A form of polyaniline.



The charge/discharge characteristics of the 1A form of polyaniline-Zn secondary batteries are also included in Table 4. Both the capacity and the energy density of the 1A form of polyaniline are superior to those of the 1S form. Investigations of electrochemical processes occurring in the 1A form of polyaniline are in progress.

References

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